Control of TiB_2 SHS Reactions by Inert Dilutions and Mechanical Constraint

Thomas Kottke
Laszlo J. Kecskes
Andrus Niiler
Ballistic Research Laboratory
Aberdeen Proving Ground, MD 21005

Self-propagating high-temperature synthesis (SHS) is a relatively new process for synthesizing some high-technology ceramic materials (Munir, 1988). For the titanium diboride system, this method involves a solid combustion reaction of mixed titanium and boron powders characterized by synthesis propagation velocities on the order of centimeters per second and reaction temperatures well in excess of 2,000°C. One advantage of the SHS process is that essentially all the heat energy required for the synthesis of these materials is supplied by the exothermic combustion reaction. This technique therefore offers the potential for energy-efficient material production. However, product materials of SHS reactions are far from fully dense, with porosity levels as high as 50%. In an effort to fabricate fully dense structural ceramic materials, the SHS process has been combined with various compaction schemes that apply pressure to the freshly synthesized material while it is still hot enough to be mechanically densified (Riley and Niiler, 1985; Holt et al., 1985; Rice et al., 1986; Niiler et al., 1990).

Although solid–solid SHS reactions are sometimes referred to as gasless reactions, due to the fact that an oxidizing atmosphere is not required, volatile impurities that are trapped on the precursor powders are expelled during the synthesis process. In the titanium diboride system, the hygroscopic nature of boron and the high SHS reaction temperature can combine to make the expulsion of volatiles particularly violent. A significant portion of the reacting sample can be eroded and carried away by the energetic volatile release, yielding a reduced amount of product material for postsynthesis densification. By using higher grade powders with relatively low impurity levels, the amount of expelled volatiles can be decreased with an associated reduction in sample mass loss. Unfortunately, powders with very low impurity levels can be very expensive and their use can nullify the potential for low-cost material production. Containment configurations have been developed which decrease sample mass loss by controlling the manner in which volatiles are expelled. However, these containment schemes generally conflict with additional packaging requirements imposed by the postsynthesis compaction apparatus.

The goal of this study was to investigate applicable methods by which the synthesis propagation velocity could be decreased in the TiB_2 system in an effort to reduce the rate at which impurity gases are expelled from the reacting sample and therefore reduce or eliminate sample material loss. A number of methods for reducing SHS propagation velocities have been previously investigated, including use of nonstoichiometric powder mixtures, use of reactant powder with larger particle size, varying the green compact density, and adding inert diluent material (Azatian et al., 1977). Off-stoichiometry powder mixtures and the use of powders with large particle sizes were not considered in this study due to the associated problems of incomplete material synthesis. Green compact density variations were also not investigated because of the processing difficulties that are inherent in handling low-density compacts and the substantial dies and pressing equipment required to make large, high-density compacts. Two velocity control methods were studied in detail: dilution of the precursor powders with inert product material and the relatively unstudied effect of sample constraint during the synthesis reaction. An additional goal was to consider the consequences of the method of propagation velocity control, such as reaction temperature reduction, on subsequent compaction processing.

Experimental Details

In order to maintain consistency between individual samples, all the Ti, B, and TiB_2 used in this investigation were from the same lots of powder. All powders were sized as −325 mesh with the titanium and crystalline boron (both, Atlantic Equipment Engineers, Bergenfield, NJ) purity levels specified as greater than or equal to 99.5% and the titanium diboride (Consolidated Astronautics, Milwaukee, WI) purity level stated as 99%. Approximately 1 kg master batches of titanium and boron

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Correspondence concerning this paper should be addressed to T. Kottke.

powders were mixed by dry ball-milling stoichiometric ratios of these powders for 3 h using ceramic containers and milling media. Smaller batches of diluted powder were then prepared by adding the required amount of titanium diboride diluent to 100 g quantities of the master batch powder and ball-milling for an additional hour. Green compacts were prepared by compacting these powder mixtures in a 2 cm dia. opposed anvil cylindrical die using 140 MPa pressure, which yielded samples 5 cm long with approximately 40% residual porosity. To aid the ignition process, a few grams of undiluted titanium and boron powder were pressed into the ignition end of the green compacts.

When reacted in a fixture that does not constrain the sample, titanium diboride samples expand in the direction normal to the synthesis front. In order to study the effect of sample expansion, two fixtures were utilized as illustrated in Figure 1. In one case the sample was held very loosely in the lateral direction by three graphite rods with no constraint in the longitudinal direction. Specimens reacted in this fixture were classified as unconstrained samples because the fixture served merely to maintain the position of the sample and did not constrain it in any way. The other fixture included a graphite end cap that prevented the reacting sample from expanding in the longitudinal sample direction. This end cap included a small hole that was aligned coaxially with the longitudinal sample axis to allow sample ignition on the top end surface. Due to the longitudinal constraint offered by this fixture, specimens reacted in this fixture were classified as constrained samples.

All synthesis reactions were performed in air. As a result, the external surfaces of reacted samples showed a characteristic TiN gold coloration that was not evident in the interior. The green compacts were held vertically during the reaction and ignited on the upper surface. A resistively heated filament, powered by a 12 V storage battery, was used to rapidly ignite a 1 g mixture of loose titanium and boron powders, which in turn ignited the powder compact. The reaction events were recorded by video camera for determination of the propagation velocity. Reaction zone positions, as measured from the unreacted end of the sample, and the associated times were measured for the central 3 cm sections of the samples. These data were least-squares fitted to a straight line to yield an average propagation velocity that was unaffected by possible edge effects or sample expansion. Thermocouples were also used in the initial testing to verify video propagation velocity measurements. Postreaction sample temperatures were recorded as a function of time using a two-color pyrometer. During temperature measurements, the pyrometer was focused on a single, centrally located external position of a sample in a constraining fixture. This arrangement avoided the complications of sample expansion during synthesis and allowed the postreaction temperature–time profile of an individual sample region to be recorded. In this configuration the temperature measurements were limited to the external surfaces of the sample. Due to heat loss from these surfaces it cannot be assumed that the measured temperatures represent internal sample temperatures; they are therefore presented as lower limits to the sample temperature.

Propagation Velocity

The reactions in both the constrained and the unconstrained samples propagated through the green compacts with velocities that decreased with increasing quantities of inert titanium diboride diluent. Figure 2 shows the dependence of propagation velocity on inert diluent concentration for both containment schemes. A similar propagation velocity dependence on diluent concentration, over the range from 10 to 20 wt. % diluent, was reported for the Ti + 2B system in a preliminary investigation by Holt et al. (1985a). In addition to the decrease in velocity with inert material, the unconstrained samples are shown to react with propagation velocities that are approximately one-third those of equivalent constrained samples. This reduced propagation velocity for samples reacted in unconstraining fixtures is attributed to transverse delamination and expansion of the product material, as discussed later.

The addition of inert titanium diboride diluent to titanium and boron powder mixtures reduces the amount of heat energy released per mole of green compact. This reduction in the amount of heat energy released during the synthesis reaction can lead to a reduction in the reaction's combustion temperature, which drives the synthesis reaction. The combustion temperature, T_c, is calculated by assuming that the enthalpy of the reactants at initial temperature T_i is equal to the enthalpy of the final product at T_c (Novikov et al., 1975). Adiabatic conditions are assumed, so that all the heat energy liberated in the synthesis reaction is assumed to heat the product to the final temperature.

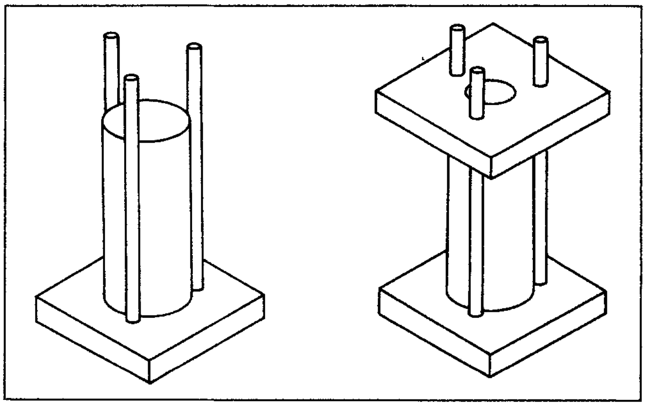

Figure 1. Reaction fixtures: left, unconstrained; right, constrained.

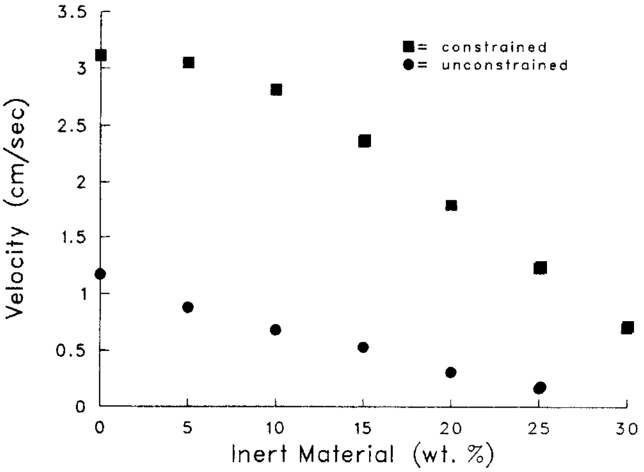

Figure 2. Effect of inert diluent on propagation velocities.

The combustion temperature for the undiluted titanium diboride system synthesized from room temperature reactants is limited to 3,193 K by the heat of fusion associated with the solid to liquid phase transition (Schick, 1966). With the addition of increasing amounts of inert titanium diboride to the precursor powders, the combustion temperature initially remains fixed at the melting temperature while reduced amounts of titanium diboride experience melting during the synthesis reaction. As the concentration of inert material exceeds 20 wt. %, the amount of melted product is reduced to zero and the combustion temperature begins to decrease linearly with increasing inert material concentration (Kottke et al., 1989). The overall dependence of the titanium diboride SHS propagation velocity in constrained samples displays a similar dependence on inert material concentration. Small additions of inert material have little effect up to a critical concentration where additional inert material leads to a linear decrease. This suggests that for these constrained samples the combustion temperature of the reacted product not only drives the propagation of the synthesis reaction but also controls its rate by determining the rate of heat transfer to the reactant material. Implicit in this description is the assumption that green compact thermal conductivities remain relatively constant with diluent concentration, making the rate of heat transfer across the reaction zone a function of reaction temperature. This conclusion is supported by the work of Azatian et al. (1977), who compared propagation velocities with experimentally measured combustion temperatures for the TiB_2 system and found a definite dependence between the velocity and the maximum combustion temperature.

The critical inert material concentration for which combustion temperatures begin to decrease is approximately 20%. The inert material concentration for which the experimentally measured propagation velocities of the constrained samples begins to decrease is only about 5 to 10%. As stated, the combustion temperature calculations assume that no heat energy is lost from the reacting system. The physical system on which the experimental measurements were made is subject to heat loss and therefore is not a strictly isolated system. Such a system that experiences heat loss requires a smaller amount of inert material to reduce the combustion temperature below the melting point of TiB_2 and would be expected to yield a lower experimental value for the critical inert material concentration value.

The source of the reduced SHS propagation velocity for TiB_2 samples reacted in nonconstraining fixtures was evident from examination of the product material. Samples reacted in nonconstraining fixtures showed extensive transverse delamination, which was not observed in samples reacted in the constraining fixture. Layering of the product material in systems with high combustion temperatures, such as the undiluted titanium diboride system, has been attributed to mechanical processes rather than the thermal processes associated with lower combustion temperature systems (Borovinskaya et al., 1974). The mechanical stresses imposed on the synthesizing material by thermal expansion of the reactant material followed by the specific volume reduction associated with the synthesis reaction lead to periodic separations along transverse isothermal planes of the reaction zone. These cracks are further expanded by the action of volatile impurities as they escape through these passages. This delamination decreases the effective thermal conductivity between the product and reactants, which in turn reduces the propagation velocity in samples reacted in the nonconstraining fixture.

Product Material

The most obvious difference between the product material reacted in constraining and nonconstraining fixtures is the expansion of the unconstrained samples along their longitudinal axes. During the synthesis reaction, the length of these samples increased by as much as 50%. The source of this longitudinal expansion is the periodic delamination of the product, discussed previously. Radial dimensions for the unconstrained samples remained nominally constant. For all dilution levels, the amount of sample mass lost from unconstrained samples during the synthesis reaction was on the order of a few percent.

By contrast, the mass lost from constrained samples ranged from only a few percent to more than 50%, as shown in Figure 3. Constrained products with low inert material concentrations had the outer radial layers of the sample blown away, leaving a fairly solid central core with extremely jagged surfaces. With increasing diluent concentration, the size of the remaining core increased, with the highest dilution products remaining essentially intact.

The driving force behind the loss of sample mass is believed to be the internal pressure created by the expulsion of volatile materials during the synthesis reactions. SHS reactions are often described as being self-purifying because the high temperatures associated with this synthesis drives water vapor and other volatile impurities from the product material. The short time scale over which these high temperatures are achieved can cause the expulsion process to be quite violent. Decreasing the rate of heating by decreasing propagation velocities is therefore expected to reduce expulsion pressures and loss of sample material. All samples that synthesized with a propagation velocity less than ≈1.5 cm/s yielded products that remained intact. For the sample geometry and compact density used in this investigation, propagation velocities below 1.5 cm/s appear to allow volatile impurities to escape at a controlled rate that is slow enough to prevent fragmentation of the TiB_2 product. The two mechanisms by which the propagation velocity has been limited, constraint and dilution, appear to be equally suited for controlling sample mass loss.

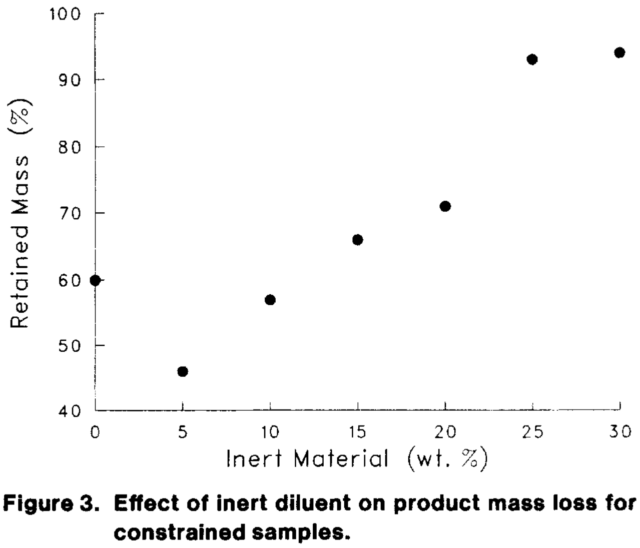

Figure 3. Effect of inert diluent on product mass loss for constrained samples.

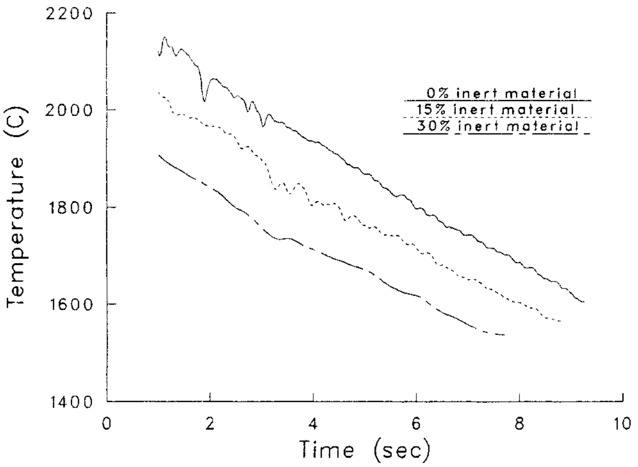

Figure 4. Effect of inert diluent on product surface temperature vs. time.

Postreaction Temperatures

Results are presented in Figure 4 for the dependence of postreaction surface temperature on inert material concentration. These data were collected on samples reacted in the constraining fixture to avoid the complications of a moving sample surface resulting from expansion during the synthesis reaction. In each case the zero of the time scale is taken to be when the synthesis zone first entered the stationary pyrometer field of view. The addition of 30% inert material reduces the surface temperature at a given postreaction time by more than 200°C compared to samples with no dilution. Another way of looking at this, which may be more applicable to postreaction processing, is that samples with 30% dilution cool to a given postreaction temperature almost 4 s earlier than undiluted samples. Thus the potentially beneficial reduction in synthesis propagation velocity made possible by the addition of inert material is accompanied by a reduction in postreaction temperature, which may prove detrimental to postreaction compaction processing.

The recorded postreaction temperatures, even for the undiluted system, are hundreds of degrees below the calculated combustion temperatures. Fast pyrometer measurements of postreaction temperatures for amorphous boron and −200 to +325 mesh titanium by Hardt and Holsinger (1973) recorded a 600°C temperature drop from maximum combustion temperatures during the first 2 s following synthesis. Thus it must be stressed that these temperature measurements are not representative of synthesis combustion temperatures but rather set a lower limit on postsynthesis sample temperatures.

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